

Enhanced electron-phonon coupling at the Mo and W (110) surfaces induced by adsorbed hydrogen

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The possible occurrence of either a charge-density-wave or a Kohn anomaly is governed by the presence of Fermi-surface nesting and the subtle interaction of electrons and phonons. Recent experimental and theoretical investigations suggest such an effect for the hydrogen covered Mo and W (110) surfaces. Using density-functional theory we examine the electronic structure and the electron-phonon coupling of these systems. Besides good agreement with the experimental phonon frequencies our study provides a characterization and quantitative analysis of an unusual scenario determining the electronic, vibrational, and structural properties of these surfaces.

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It is well established that the vibrational spectra of some transition-metal *crystals* exhibit more or less pronounced anomalous properties. For example, in the phonon band structure of bulk Mo a clear dip occurs at the H -point [1,2]. Several theoretical studies [3,4,5,6,7] support the idea that these anomalies are directly related to a nesting of the Fermi surface [8].

If the electron-phonon (e - ph) coupling and the Kohn anomaly become strong, an instability will arise, leading to a Peierls-type, or more generally to a charge-density-wave (CDW) type of insulator. The new ground state then contains a frozen-in periodic lattice distortion. The distortion lowers the kinetic energy of electrons near the Fermi surface through an energy gap, which acts as the CDW order parameter. In systems of effectively reduced dimensionality, such as layer and chain bulk compounds, and crystal surfaces, one expects nesting, and thus the occurrence of either strong Kohn anomalies, or of a proper CDW ground state, to be generally enhanced [9]. Nonetheless, with the exception of W(100) and Mo(100) [10], no well-established cases of either giant Kohn anomalies *or* of surface CDW's have yet emerged on real crystal surfaces.

The discovery of extremely sharp and deep indentations in the surface phonon spectra of H/Mo(110) and H/W(110) at full hydrogen coverage [11,12] has therefore come as a surprise, raising much interest, and many questions. The anomalies are seen at an incommensurate \mathbf{k} -point, \mathbf{Q}_{c1} , along the [001] direction ($\overline{\Gamma H}$) and, somewhat less visibly but also unmistakably, at the commensurate

zone boundary point $\mathbf{Q}_{c2} = \overline{S}$ of the surface Brillouin zone. Out of the ordinary Rayleigh mode, *two* simultaneous anomalies appear to develop at these two \mathbf{k} -points. One, ω_1 , is extremely deep and sharp, and is only seen by helium atom scattering (HAS). The other, ω_2 , is instead soft and mild, and is observed by both HAS and high resolution electron energy loss spectroscopy (HREELS) [13]. The agreement between HAS and HREELS dispersion curves of the mild anomaly ω_2 supports the idea that this indentation is associated with the Rayleigh wave. The interpretation of the deep and sharp anomaly is less straightforward. A close link between the surface phonon anomalies and hydrogen vibrations [13] seems to be ruled out, since the HAS spectra remain practically unchanged when deuterium is adsorbed instead of hydrogen [11,12].

Recent density-functional-theory calculations of the Fermi surface of the hydrogen-covered Mo(110) (1×1) surface identified a hydrogen adsorption induced quasi-one-dimensional Fermi-surface nesting in two different directions [14,15]. The calculated nesting vectors $\mathbf{Q}_{c1}^{\text{th}}$ along $\overline{\Gamma H}$ and $\mathbf{Q}_{c2}^{\text{th}}$ along $\overline{\Gamma S}$ are in excellent agreement with the critical wave vectors at which HAS detected the anomalous behavior.

These experimental and theoretical results leave *two* possible scenarios still open for the ground state of these surfaces, namely:

- A. The surface e - ph coupling is very strong, the Rayleigh-wave frequency at $2\mathbf{k}_F$ becomes *imaginary*, and the surface is unstable. A stabilizing distortion takes place and the true ground state of the surface is a quasi-one-dimensional CDW, incommensurate along $\overline{\Gamma H}$, and commensurate along $\overline{\Gamma S}$. In this hypothesis, suggested in Ref. [10], the surface phonon anomalies ω_1 and ω_2 are therefore identified as phase and amplitude CDW modes, well studied in one-dimensional cases [16,17].
- B. The e - ph coupling and the associated Kohn anomaly ω_2 are only moderate. Therefore, the unreconstructed surface structure remains stable and the electronic instability is not removed. One should find only a slight downward shift of the Rayleigh-wave frequency which remains *real*. Within this picture, which was put forward in

Ref. [14], the mode ω_2 is predominantly phonon-like and the other mode, ω_1 , is predominantly due to an electron-hole excitation.

Each of the two possibilities would be interesting and uncommon. In order to ascertain whether scenario A or scenario B is actually realized, a microscopic calculation of the relevant *e-ph* coupling, and of the ensuing shifts of surface phonon frequencies, is needed. A frozen-phonon calculation at \mathbf{Q}_{cl} is out of question, due to incommensurability. Luckily, point \bar{S} is instead simply commensurate, and here the calculations are feasible.

We performed density functional theory calculations using the local-density approximation for the exchange-correlation energy functional [18,19]. For the self-consistent solution of the Kohn-Sham equations we employed the full-potential linearized augmented plane-wave method [20]. Our code enables the direct calculation of atomic forces [21] and, with a damped Newton dynamics scheme, the efficient determination of the relaxed atomic structure [22]. The substrates are modeled by five and seven layer slabs repeated periodically and separated by a vacuum region of thickness equivalent to four substrate layers. For the potential the (l, m) representation within each muffin tin (MT) sphere is taken up to $l_{\max} = 3$ while the kinetic-energy cutoff for the interstitial region is set to 64 Ry. We choose the plane-wave cutoff for the wavefunctions to be 12 Ry and employ a (l, m) representation in the MTs with $l_{\max} = 8$ for them. The MT radii for the W and Mo atoms are chosen to be 1.27 Å. For the hydrogen this radius is set to 0.48 Å. Fermi smearing with a broadening of $kT_{el} = 0.07$ eV is used in order to stabilize self-consistency and \mathbf{k} summation [23]. In the case of the W surfaces the valence and semi-core (core) electrons are treated scalar (fully) relativistically while for Mo all electrons are treated non-relativistically. The in-plane lattice constants 3.14 Å (W) and 3.13 Å (Mo) calculated without including zero-point vibrations are in good agreement with the respective measured bulk lattice parameters (3.163 Å and 3.148 Å for W [24] and Mo [25], respectively) at room temperature.

The necessary first step of our study is to determine the atomic and electronic structures of the clean and hydrogen-covered (110) surfaces. In Table I we summarize the calculated relaxation parameters for these systems. It turns out that the results for W(110) are very similar to those obtained for Mo(110). The investigations shine light on a long-standing problem concerning the structure of W(110) covered with more than half a monolayer of hydrogen. For this system Estrup's group observed a symmetry change in the low energy electron diffraction pattern and proposed that this might be caused by a displacement of the top layer W atoms along the $[\bar{1}10]$ direction [26]. Similar studies for H/Mo(110) did not provide any evidence for such a top-layer-shift reconstruction [27]. For both adsorbate systems we per-

formed several structure optimizations starting from different trial configurations in order to check whether such a reconstruction is energetically favorable. It turns out that for both substrates the hydrogen atom relaxes into a quasi-threefold position (indicated as H in Fig. 1 in Ref. [14,15]), and that the adsorption reduces the inward relaxation of the clean surface considerably. Furthermore, for H/Mo(110) [14,15] as well as H/W(110) [28] we find no evidence for a *pronounced* top-layer-shift reconstruction. However, y_1 is non-zero, but very small, for both adsorbate systems, which indicates an anisotropic vibration of the top layer parallel to the substrate with a favorable direction along $[\bar{1}10]$.

The similarities between Mo(110) and W(110) continue when we compare the electronic structure of the relaxed surface systems. For both systems the H adsorption alters the surface potential and induces a shift of the $(d_{3z^2-r^2}, d_{xz})$ band to higher binding energies [14,15,28]. In this way the Fermi line associated with this band is moved away from $\bar{\Gamma N}$ into a band gap of the surface projected band structure, and the respective states become true surface states. For both adsorbate systems the shifted $(d_{3z^2-r^2}, d_{xz})$ band is characterized by a high density of states at the Fermi level, and the new Fermi contour gives rise to a nesting [14,28]. The magnitudes of the calculated and measured critical wavevectors along $\bar{\Gamma S}$ and $\bar{\Gamma H}$ are listed in Table II. The agreement between theory and experiment for both systems is excellent.

The experimental phonon spectra of the (110) surfaces of Mo and W show two distinct reactions to the adsorption of hydrogen. Along $\bar{\Gamma H}$ and $\bar{\Gamma S}$ a monolayer of hydrogen induces a softening of the Rayleigh and (to a smaller amount) of the longitudinal [29] wave while a stiffening of these modes is observed along $\bar{\Gamma N}$. Our goal is to investigate both effects theoretically.

A frozen phonon calculation at \bar{S} is particularly convenient, since at the zone boundary the Rayleigh-wave polarization is purely vertical, and the second layer is immobile by symmetry. In fact, at \bar{S} the Rayleigh wave is not embedded in the projected bulk phonon bands and thus it is strongly localized at the surface. Moreover, we find that the hydrogen vibrations are of no significant importance for the calculated phonon frequencies.

In order to make our frozen phonon studies computationally feasible we use an enlarged surface unit cell together with a five layer slab and reduce the plane-wave cutoff for the wave functions to 10 Ry (the convergence of total energy differences was tested). The geometries are defined by the five layer relaxation parameters presented in Table I. One should mention that some relaxation parameters, i.e., Δd_{ij} , change considerably when we perform a calculation with a slab of five instead of seven metal layers. We note, however, that the values of the critical wavevectors and the position of the hydrogen with respect to the substrate surface are practically insensitive to the thickness of the slab. This indicates

that the physical properties we are interested in, e.g. the nesting features, are well localized surface phenomena and that the results of our five layer slab studies can be trusted.

The phonon frequency was evaluated using the harmonic term of a fourth-order polynomial fit to the total energy changes. The total energies were calculated for five displacements between 0% and 3.6% of the (110) surface interlayer spacing. One might expect that the calculated frequencies, especially the one for the \bar{S} -point phonon, are sensitive to the Brillouin-zone sampling. For instance, for the study of the (2×1) reconstructions of the diamond (111) surface Vanderbilt and Louie [30] employed a \mathbf{k} -point mesh which becomes logarithmically denser close to the zone boundary. We performed test calculations using 16, 56, and 120 \mathbf{k} -points in the surface Brillouin zone in order to test the convergence of our results, and found that a uniform \mathbf{k} -point mesh of 56 points is sufficient. The calculated frequencies are collected in Table III. At the \bar{N} point our results reproduce the experimentally observed *stiffening* of the Rayleigh-wave frequency as hydrogen is adsorbed. This agreement encourages to go on to the study of the \bar{S} -point Rayleigh wave. Here we find that the stiffening effects are over-compensated because of a strong interaction between the phonons and the electron states at the Fermi level. In our calculations this leads to a moderate *lowering* of the phonon energy by 5.5 meV for Mo and 6.1 meV for W, in good agreement with the experimental results. This strongly supports the conclusion that scenario B is the correct one.

We may extract the surface *e-ph* coupling at the \bar{S} point by calculating the splitting of the two Kohn-Sham eigenvalues folded back at the point midway between $\bar{\Gamma}$ and \bar{S} as a function of the nuclear displacement. We obtain the gain in electronic energy which arises from the lattice distortion of the frozen phonon, and this quantity can be related to the electron-phonon interaction at the surface. The calculated splitting $2\Delta\epsilon$ is practically linear in the nuclear displacement and the coefficient of the linear relation is 2.81 ± 0.10 eV/Å for Mo and 4.41 ± 0.06 eV/Å for W. The larger value for W reflects a more efficient coupling between the electrons and phonons and suggests that the anomaly in the phonon band of W(110) should be more pronounced. This is indeed confirmed by the HAS experiments, which find that the deeper dip is wider on H/W(110) than on H/Mo(110). Furthermore, Hulpke and Lüdecke [11,12] reported the occurrence of small structures in the HAS diffraction pattern for H/W(110) at the critical wavevector. These features, which were not observed for the Mo substrate, might indicate the start up of the formation of a CDW at W(110).

Our calculations of the electron-phonon interaction at the (110) surfaces of both Mo and W and their changes due to hydrogen adsorption pinpoint the phonon character of the small anomaly ω_2 and identify the subtle

interplay between the electronic structure and the vibrational spectra of the transition metal surfaces. The results clearly support the interpretation that the small dip observed by HAS and HREELS is due to a Kohn anomaly, while the huge dip arises from an electron-hole excitation. Thus, scenario B is operative. There are in fact two independent experimental hints which support our conclusion. If picture A were correct, and ω_1 a phason, that phason should exist at an incommensurate point like \mathbf{Q}_{c1} , but should be absent at the zone-boundary commensurate point $\mathbf{Q}_{c2} = \bar{S}$ [16]. However, data near \bar{S} clearly indicate a lower branch at that point too. Only if scenario B holds, is a second branch expected at \bar{S} due to an electron-hole excitation and a good Fermi-surface nesting. Furthermore, recent HREELS experiments [29] reveal a positive temperature dependence of the small indentation ($d\omega_2/dT > 0$) consistent with that of a Kohn anomaly, i.e., a weakening of the anomaly with increasing temperature.

In conclusion, we have discussed the atomic and electronic structures of the clean and H-covered Mo(110) and W(110) surfaces and studied the changes in the vibrational properties of these surface systems upon hydrogen adsorption. Two decisive experimental findings could be reproduced: At the symmetry point \bar{N} the Rayleigh phonon mode is *stiffened* by the hydrogen adsorption, whereas for the \bar{S} -point Rayleigh wave we obtain a *weakening* of the phonon energy due to Fermi-surface nesting. The calculations support the interpretation [14] that scenario B is in effect (the Kohn anomaly picture), as opposed to the CDW picture [10] (scenario A). Thus, the modest anomaly seen in HAS and HREELS is a predominantly phonon-like excitation, and the giant indentation, seen only in HAS, is predominantly due to an excitation of electron-hole pairs. The various elements identified in our analysis could be combined in a future study of the behavior of the H adatoms in order to analyze their liquid-like state features observed in the HREELS measurements [13].

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- [1] B. N. Powell, P. Martel, and A. D. B. Woods, Phys. Rev. **171**, 727 (1968).
 - [2] J. Zaretsky, C. Stassis, B. N. Harmon, K. M. Ho, and C. L. Fu, Phys. Rev. B **28**, 697 (1983).
 - [3] K. M. Ho, C. L. Fu, B. N. Harmon, W. Weber, and D. R. Hamann, Phys. Rev. Lett. **49**, 673 (1982).
 - [4] K. M. Ho, C. L. Fu, and B. N. Harmon, Phys. Rev. B **29**,

1575 (1984).

- [5] Y. Chen, C. L. Fu, K. M. Ho, and B. N. Harmon, Phys. Rev. B **31**, 6775 (1985).
- [6] C. L. Fu, K. M. Ho, B. N. Harmon, and S. H. Liu, Phys. Rev. B **28**, 2975 (1983).
- [7] D. Singh and H. Krakauer, Phys. Rev. B **43**, 1441 (1991).
- [8] C. M. Varma and W. Weber, Phys. Rev. Lett. **39**, 1094 (1977); Phys. Rev. B **19**, 6142 (1979).
- [9] E. Tosatti, Festkörperprobleme **15**, 113 (1975).
- [10] E. Tosatti, to be published in: *Electronic Surface and Interface States on Metallic Systems*, eds. E. Bertel and M. Donath (World Scientific, Singapore, 1995).
- [11] E. Hulpke and J. Lüdecke, Phys. Rev. Lett. **68**, 2846 (1992); J. Electron. Spectr. Relat. Phenom. **64/65**, 641 (1993).
- [12] J. Lüdecke, Ph.D. thesis, Universität Göttingen(1994).
- [13] M. Balden, S. Lehwald, H. Ibach, and D. L. Mills, Phys. Rev. Lett. **73**, 854 (1994).
- [14] B. Kohler, P. Ruggerone, S. Wilke, and M. Scheffler, Phys. Rev. Lett. **74**, 1387 (1995).
- [15] P. Ruggerone, B. Kohler, S. Wilke, and M. Scheffler, to be published in: *Electronic Surface and Interface States on Metallic Systems*, eds. E. Bertel and M. Donath (World Scientific, Singapore, 1995).
- [16] P. A. Lee, T. M. Rice, and P. W. Anderson, Solid State Commun. **14**, 703 (1974).
- [17] G. Giuliani and E. Tosatti, Il Nuovo Cimento **47**, 135 (1978); and in: *Quasi One-Dimensional Conductors I*, eds. S. Barišić, A. Bjeliš, J. R. Cooper and B. Leontić (Springer Verlag, Berlin, Heidelberg, New York 1979), p. 191.
- [18] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
- [19] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
- [20] P. Blaha, K. Schwarz, P. Sorantin, and S. B. Trickey, Comput. Phys. Commun. **59**, 399 (1990); P. Blaha, K. Schwarz, R. Augustyn, WIEN93, Technische Universität Wien, 1993.
- [21] R. Yu, D. Singh, and H. Krakauer, Phys. Rev. B **43**, 6411 (1991).
- [22] B. Kohler, S. Wilke, and M. Scheffler, Comput. Phys. Commun., in print.
- [23] J. Neugebauer and M. Scheffler, Phys. Rev. B **46**, 16067 (1992).
- [24] J. S. Shah and M. E. Straumanis, J. Appl. Phys. **42**, 3288 (1971).
- [25] K. W. Katahara, M. H. Manghnani, and E. S. Fisher, J. Phys. F **9**, 773 (1979).
- [26] J. W. Chung, S. C. Ying, and P. J. Estrup, Phys. Rev. Lett. **56**, 749 (1986).
- [27] M. Altman, J. W. Chung, P. J. Estrup, J. M. Kosterlitz, J. Prybyla, D. Sahu, and S. C. Ying, J. Vac. Sci. Technol. **A** 5, 1045 (1987).
- [28] B. Kohler, P. Ruggerone, and M. Scheffler, to be published.
- [29] M. Balden, private communication.
- [30] D. Vanderbilt and S. G. Louie, Phys. Rev. B **30**, 6118 (1984).

TABLE I. Calculated relaxation parameters for the clean and H-covered (110) surfaces of Mo and W. The height of the hydrogen above the surface and its $\bar{1}10$ offset from the [001] bridge position are denoted by d_H and y_H , respectively. The shift of the surface layer with respect to the substrate is y_1 . The parameters Δd_{ij} describe the percentage change of the interlayer distance between the i -th and the j -th substrate layers with respect to the bulk interlayer spacing d_0 . For each system the results for a five layer (first line) and for a seven layer (second line) slab are presented.

system	y_H (Å)	d_H (Å)	y_1 (Å)	Δd_{12} (% d_0)	Δd_{23} (% d_0)	Δd_{34} (% d_0)
Mo(110)	—	—	—	-5.9	-0.8	—
	—	—	—	-4.5	+0.5	0.0
H/Mo(110)	0.63	1.08	0.05	-2.7	-0.4	—
	0.60	1.07	0.03	-2.1	+0.1	-0.1
W(110)	—	—	—	-4.1	-0.2	—
	—	—	—	-3.3	-0.2	-0.6
H/W(110)	0.68	1.21	0.01	-1.3	0.0	—
	0.67	1.20	0.05	-1.3	+0.3	+0.4

TABLE II. Theoretical Fermi surface nesting vectors compared to critical wavevectors obtained by HAS and HREELS experiments [11,12,13].

direction	system	$ \mathbf{Q}_c $ (Å ⁻¹)	
		theory	experiment
$\Gamma\bar{H}$	H/Mo(110)	0.86	0.90
	H/W(110)	0.96	0.95
$\Gamma\bar{S}$	H/Mo(110)	1.23	1.22
	H/W(110)	1.22	1.22

TABLE III. Comparison of calculated frozen phonon energies and experimental results values obtained by HAS [11,12] and HREELS [13]. The numerical accuracy of the theoretical phonon energies is about ± 1 meV.

phonon	system	E_{ph} (meV)	
		theory	experiment
N	W(110)	17.0	14.5
	H/W(110)	19.8	~19
\bar{S}	Mo(110)	23.7	~21
	H/Mo(110)	18.2	<16
	W(110)	19.1	16.1
	H/W(110)	13.0	11